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(54) PROCESS FOR PRODUCING 1,1,1,3,3-PENTAFLUOROPROPANE, PROCESS FOR
PRODUCING 2,2,3-TRICHLORO-1,1,1,3,3-PENTAFLUOROPROPANE, AND PROCESS FOR
PRODUCING 2,2,3-TRICHLORO-1,1,1-TRIFLUOROPROPANE

(57) 1,1,1,3,3-pentafluoropropane is produced by hydrogenating 2,2,3-trichloro-1,1,1,3,3-pentafluoropropane with at least 4.5 times by equivalent as much hydrogen in the presence of a noble metal catalyst, particularly a palladium catalyst in vapor phase. The 1,1,1,3,3-pentafluoropropane is also produced by chlorofluorinating propane, propene, hexachloropropene, etc., in the presence of a metallic catalyst into 2,2,3-trichloro-1,1,1,3,3-pentafluoropropane and reducing the product with hydrogen in the presence of a noble metal catalyst. It is possible to produce 2,2,3-trichloro-1,1,1,3,3-pentafluoropropane and 1,1,1,3,3-pentafluoropropane efficiently and economically.

DescriptionIndustrial use

5 This invention pertains to the process of manufacturing 1,1,1,3,3-pentafluoropropane (HFC245fa), a useful compound which may become a substitute compound for CFC and HCFC used as refrigerant, blowing agent and cleaner, in more detail to the process of manufacturing 1,1,1,3,3-pentafluoropropane with 2,2,3-trichloro-1,1,1,3,3-pentafluoropropane (CFC215aa) as an intermediate, to the process of manufacturing 2,2,3-trichloro-1,1,1,3,3-pentafluoropropane (CFC215aa), an intermediate of HFC245fa, and to the process of manufacturing 2,3,3-trichloro-1,1,1-trifluoropropene, an intermediate of CFC215aa.

Prior art

1,1,1,3,3-pentafluoropropane (HFC245fa) is a useful compound as a substitute for freon used as a blowing agent, refrigerant, cleaner, etc.

As the process of manufacturing 1,1,1,3,3-pentafluoropropane (HFC245fa), a method is known under which 2,2,3-trichloro-1,1,1,3,3-pentafluoropropane (CFC215aa) is used as a raw material, which is reduced with a palladium catalyst supported on activated carbon using 3 to 4 equivalent parts of hydrogen to the raw material (U.S. Patent No.2942036).

Manufacturing HFC245fa using CFC215aa involves two broad categories of problems. The first problem is how efficiently and economically CFC215aa is manufactured, and the second problem is how efficiently CFC215aa is reduced to obtain HFC245fa.

Regarding the first problem, it is important to select a low-priced starting material and to efficiently convert it into CFC215aa. There have been several reports on techniques of using low-price available compound with carbon number of 3 as a starting material, then chlorine-fluorinating it to obtain $\text{CF}_3\text{CFC1CF}_3$.

Japanese Patent Opening No. 145033/92 discloses a process of manufacturing $\text{CF}_3\text{CFC1CF}_3$ in which propane and propylene, etc. are chlorofluorinated to generate a perhalogenated C_3 chlorofluoro compound, and this compound is fluorinated.

Japanese Patent Opening No. 117335/92 discloses a process in which propane and propylene, etc. are chlorine-fluorinated to generate $\text{CF}_3\text{CC1}=\text{CC1}_2$, and this compound is further chlorine-fluorinated to form $\text{CF}_3\text{CFC1CF}_3$. Japanese Patent Opening No. 108746/92 discloses a process in which hexachloropropene is chlorofluorinated to generate a perhalogenated C_3 chlorofluoro compound and this compound is fluorinated to form $\text{CF}_3\text{CFC1CF}_3$.

However, these processes are designed to obtain $\text{CF}_3\text{CFC1CF}_3$ (a C_3 compound with 7 fluorine atoms and 1 chlorine atom), and the application of these processes to the manufacture of $\text{CF}_3\text{CC1}_2\text{CF}_2\text{C1}$ (a C_3 compound with 5 fluorine atoms and 3 chlorine atoms) (CFC215aa) produces a large amount of by-product which are too fluorinated, thus not only producing a low yield rate, but also making it impossible to reuse the by-product as a raw material for manufacturing CFC215aa. A method of synthesizing the conditions suitable for the manufacture of CFC215aa therefore needs to be developed.

Regarding the second problem, that is, the reduction of CFC215aa, the above U.S. patented process provides only a maximum 60% yield rate to HFC245fa, the subject-matter, and also produces a large amount of 1,1,3,3,3-pentafluoropropene, which is not suitable for industry. Consequently, an efficient process of reducing CFC215aa into HFC245fa needs to be developed.

Object of invention

45 The object of this invention is to provide a process to efficiently and economically manufacture 1,1,1,3,3-pentafluoropropane, especially a process of manufacturing 1,1,1,3,3-pentafluoropropane at a high yield rate in the reductive reaction of 2,2,3-trichloro-1,1,1,3,3-pentafluoropropane.

The other object of this invention is to provide a process to efficiently and economically manufacture 2,2,3-trichloro-1,1,1,3,3-pentafluoropropane and 2,3,3-trichloro-1,1,1-trifluoropropene as intermediates in the manufacture of 1,1,1,3,3-pentafluoropropane.

Constitution of invention

55 This inventors have investigated in detail the process of manufacturing 1,1,1,3,3-pentafluoropropane, and have discovered that the reduction of 2,2,3-trichloro-1,1,1,3,3-pentafluoropropane, when used as a raw material as in the past at not more than 4 equivalent parts of hydrogen by the vapor phase method in the presence of a noble metal catalyst, especially a palladium catalyst, provides the subject-matter at a low yield rate, while reduction using not less than 4.5 equivalent parts of hydrogen provides the subject-matter at a high yield and selection rates, thus leading to completion of the present invention.

This invention pertains to the process of manufacturing 1,1,1,3,3-pentafluoropropane, including a process in which 2,2,3-trichloro-1,1,1,3,3-pentafluoropropane is allowed to react with not less than 4.5 equivalent parts of hydrogen to 2,2,3-trichloro-1,1,1,3,3-pentafluoropropane to be hydrogen-reduced by the vapor phase method in the presence of a noble metal catalyst.

In the manufacturing process based on this invention, 2,2,3-trichloro-1,1,1,3,3-pentafluoropropane in particular is used as the raw material, to which not less than 4.5 equivalent parts (particularly 4.5 to 10 equivalent parts) of hydrogen is used to allow to react with hydrogen added particularly at temperatures of 100 °C to 350°C by the vapor phase method in the presence of a palladium catalyst, which permits the manufacture of 1,1,1,3,3-pentafluoropropane at a high yield rate of 90% or more.

The usable vapor phase reaction methods include the fixed bed vapor phase reaction method and the fluidized bed vapor phase reaction method.

It is preferable that the palladium catalyst is supported on a carrier composed of at least one carrier selected from among activated carbon, alumina, silica gel, titanium oxide and zirconia.

The grain size of the carrier hardly affects the reaction, but a size of 0.1mm to 100mm is preferred.

The usable range of supporting concentrations varies widely from 0.05% to 10% by weight, but usually a carrier at 0.5% to 5% by weight is recommended.

The reaction temperature is normally 100°C to 350°C, preferably 200°C to 300°C.

In the hydrogen reduction reaction of 2,2,3-trichloro-1,1,1,3,3-pentafluoropropane on the basis of this invention, the ratio of hydrogen to the raw material can be widely varied if hydrogen is not less than 4.5 equivalent parts to 2,2,3-trichloro-1,1,1,3,3-pentafluoropropane. Usually, however, 1.5 to 3 times as much hydrogen as the stoichiometric quantity is used to ensure hydrogenation. To the starting substance of the total mol, a considerably greater quantity of hydrogen than the stoichiometric quantity, 10 mols or more, for example, may be used. Excess hydrogen can be recovered and reused.

The reaction pressure is not particularly restricted, and applied pressure, reduced pressure, and atmospheric pressure may be used, but reaction under applied or atmospheric pressure is preferred.

The contact time is usually 0.1s to 300s, typically 1s to 30s.

This invention also provides a process of manufacturing 1,1,1,3,3-pentafluoropropane including processes (1) and (2) as follows:

(1) A process in which hexachloropropene is allowed to react with hydrogen fluoride (HF) and chlorine in the presence of a chromium or aluminum catalyst by the vapor phase method, or in the presence of an antimony catalyst by the liquid phase method to obtain 2,2,3-trichloro-1,1,1,3,3-pentafluoropropane.

(2) Then, a process in which this 2,2,3-trichloro-1,1,1,3,3-pentafluoropropane is allowed to react with not less than 4.5 equivalent parts of hydrogen to this 2,2,3-trichloro-1,1,1,3,3-pentafluoropropane to be hydrogen-reduced in the presence of a noble metal catalyst by the vapor phase method, obtaining 1,1,1,3,3-pentafluoropropane.

This invention also provides the process of manufacturing 1,1,1,3,3-pentafluoropropane including processes (1), (2) and (3) as follows:

(1) A process in which hexachloropropene is allowed to react with hydrogen fluoride (HF) in the presence of an aluminum catalyst by the vapor phase method to obtain 2,3,3-trichloro-1,1,1-trifluoropropene.

(2) Then, a process in which this 2,3,3-trichloro-1,1,1-trifluoropropene is allowed to react with hydrogen fluoride (HF) and chlorine in the presence of at least one metal catalyst selected from a group composed of chromium, iron, cobalt, zinc, copper and manganese by the vapor phase method, or in the presence of an antimony catalyst by the liquid phase method to obtain 2,2,3-trichloro-1,1,1,3,3-pentafluoropropane.

(3) Then, a process in which this 2,2,3-trichloro-1,1,1,3,3-pentafluoropropane is allowed to react with not less than 4.5 equivalent parts of hydrogen to 2,2,3-trichloro-1,1,1,3,3-pentafluoropropane in the presence of a noble metal catalyst by the vapor phase method to be hydrogen-reduced, obtaining 1,1,1,3,3-pentafluoropropane.

This invention also provides the process of manufacturing 1,1,1,3,3-pentafluoropropane including processes (1) and (2) as follows:

(1) A process in which at least a kind selected from a group composed of 2,3,3-trichloro-1,1,1-trifluoropropene, 1,2,3,3-tetrachloro-1,1-difluoropropene, and 1,1,2,3,3-pentachloro-1-fluoropropene is allowed to react with hydrogen fluoride (HF) and chlorine in the presence of at least one metal catalyst selected from a group composed of chromium, iron, cobalt, zinc, copper and manganese by the vapor phase method, or in the presence of an antimony catalyst by the liquid phase method to obtain 2,2,3-trichloro-1,1,1,3,3-pentafluoropropane.

(2) Then, a process in which this 2,2,3-trichloro-1,1,1,3,3-pentafluoropropane is allowed to react with not less than 4.5 equivalent parts of hydrogen to 2,2,3-trichloro-1,1,1,3,3-pentafluoropropane to be hydrogen-reduced by the vapor phase method in the presence of a noble metal catalyst, obtaining 1,1,1,3,3-pentafluoropropane.

5 This invention also provides a process of manufacturing 1,1,1,3,3-pentafluoropropane including processes (1) and (2) as follows:

(1) A process in which at least one compound selected from a group composed of propane, propylene, and partially halogenated an acyclic hydrocarbon with a carbon number of 3 is allowed to react with hydrogen fluoride (HF) and chlorine in the presence of chromium and/or iron catalyst(s) by the vapor phase method to obtain 2,2,3-trichloro-1,1,1,3,3-pentafluoropropane.

(2) Then, a process in which this 2,2,3-trichloro-1,1,1,3,3-pentafluoropropane is allowed to react with not less than 4.5 equivalent parts of hydrogen to 2,2,3-trichloro-1,1,1,3,3-pentafluoropropane in the presence of a noble metal catalyst by the vapor phase method to be hydrogen-reduced, obtaining 1,1,1,3,3-pentafluoropropane.

15 This invention also provides a process of manufacturing 1,1,1,3,3-pentafluoropropane including processes (1), (2) and (3) as follows:

(1) A process in which at least one compound selected from a group composed of propane, propylene and partially halogenated acyclic hydrocarbon with carbon number of 3 is allowed to react with hydrogen fluoride (HF) and chlorine in the presence of at least one metal catalyst selected from a group composed of aluminum, copper, cobalt, zinc and manganese by the vapor phase method to obtain 2,3,3-trichloro-1,1,1-trifluoropropene.

(2) Then, a process in which this 2,3,3-trichloro-1,1,1-trifluoropropene is allowed to react with hydrogen fluoride (HF) and chlorine in the presence of at least one metal catalyst selected from a group composed of chromium, iron, cobalt, zinc, copper and manganese by the vapor phase method, or in the presence of an antimony catalyst by the liquid phase method to obtain 2,2,3-trichloro-1,1,1,3,3-pentafluoropropane.

(3) Then, a process in which this 2,2,3-trichloro-1,1,1,3,3-pentafluoropropane is allowed to react with not less than 4.5 equivalent parts of hydrogen to 2,2,3-trichloro-1,1,1,3,3-pentafluoropropane to be hydrogen-reduced in the presence of noble metal catalyst(s) by the vapor phase method, obtaining 1,1,1,3,3-pentafluoropropane.

30 This invention also provides a process of manufacturing 2,2,3-trichloro-1,1,1,3,3-pentafluoropropane including a process in which hexachloropropene is allowed to react with hydrogen fluoride (HF) and chlorine in the presence of chromium and/or aluminum catalyst(s) by the vapor phase method, or in the presence of an antimony catalyst by the liquid phase method.

35 This invention also provides a process of manufacturing 2,2,3-trichloro-1,1,1,3,3-pentafluoropropane including processes (1) and (2) as follows:

(1) A process in which hexachloropropene is allowed to react with hydrogen fluoride (HF) in the presence of an aluminum catalyst by the vapor phase method to obtain 2,3,3-trichloro-1,1,1-trifluoropropene.

40 (2) Then, a process in which this 2,3,3-trichloro-1,1,1-trifluoropropene is allowed to react with hydrogen fluoride (HF) and chlorine in the presence of at least one metal catalyst selected from a group composed of chromium, iron, cobalt, zinc, copper and manganese by the vapor phase method, or in the presence of an antimony catalyst by the liquid phase method to obtain 2,2,3-trichloro-1,1,1,3,3-pentafluoropropane.

45 This invention also provides a process of manufacturing 2,2,3-trichloro-1,1,1,3,3-pentafluoropropane including a process in which at least one selected from a group composed of 2,3,3-trichloro-1,1,1-trifluoropropene, 1,2,3,3-tetrachloro-1,1-difluoropropene and 1,1,2,3,3-pentachloro-1-fluoropropene is allowed to react with hydrogen fluoride (HF) and chlorine in the presence of at least one metal catalyst selected from a group composed of chromium, iron, cobalt, zinc, copper and manganese by the vapor phase method, or in the presence of an antimony catalyst by the liquid phase method to obtain 2,2,3-trichloro-1,1,1,3,3-pentafluoropropane.

50 This invention further provides a process of manufacturing 2,3,3-trichloro-1,1,1-trifluoropropene, including a process in which hexachloropropene is allowed to react with hydrogen fluoride (HF) in the presence of an aluminum catalyst by the vapor phase method.

55 In the above processes of manufacturing on the basis of this invention, the following preferable routes may be adopted in order to obtain CFC215aa as an intermediate in manufacturing 1,1,1,3,3-pentafluoropropane (HFC245fa) by manufacturing 2,2,3-trichloro-1,1,1,3,3-pentafluoropropane (CFC215aa) first, and then hydrogen-reducing the compound.

Method A: Hexachloropropene is used as the starting substance, and this compound is allowed to react with HF and chlorine to be chlorofluorinated, obtaining CFC215aa directly.

Method B: Hexachloropropene is used as the starting substance, and this compound is allowed to react with HF to be fluorinated, generating 2,3,3-trichloro-1,1,1-trifluoropropene, then the compound is allowed to react with HF and chlorine to be chlorofluorinated, obtaining CFC215aa.

Method C: At least one selected from a group composed of 2,3,3-trichloro-1,1,1-trifluoropropene, 1,2,3,3-tetrachloro-1,1-difluoropropene, and 1,1,2,3,3-pentachloro-1-fluoropropene is used as the starting substance, and this compound is chlorofluorinated with HF and chlorine to obtain CFC215aa.

Method D: Propane, propylene and/or partially halogenated acyclic hydrocarbon with carbon number of 3 is used as the starting substance, and this compound is allowed to react with HF and chlorine to be chlorofluorinated, obtaining CFC215aa directly.

Method E: Propane, propylene and/or partially halogenated acyclic hydrocarbon with carbon number of 3 is used as the starting substance, and this compound is allowed to react with HF and chlorine to be chlorofluorinated first, generating 2,3,3-trichloro-1,1,1-trifluoropropene, then the compound is allowed to react with HF and chlorine to be chlorofluorinated, obtaining CFC215aa.

In Method A, hexachloropropene is used as the starting substance to be chlorofluorinated with hydrogen fluoride and chlorine, either by the vapor phase method or the liquid phase method.

The catalyst in the vapor phase method includes chromium and/or aluminum. These catalysts can be used in the form of a salt such as the hydroxide, chloride, nitrate or oxide of the metal. These catalysts can also be used in a condition where the above metals are supported on a carrier such as activated carbon. The supporting quantity of metal catalyst on the carrier is not particularly restricted, but preferably not be less than 0.1% by weight. The supporting method on the carrier in general is such that a metal compound normally in the form of a water soluble salt such as nitrate is dissolved in the ion-exchanged water in which the carrier is soaked, and the water content is removed by distillation to obtain the desired catalyst.

The catalyst is preferably be treated for fluorination prior to starting the reaction. A preferable fluorination method is to bring the catalyst into contact with HF at a temperature not less than that provided for reaction, but an excessively high temperature will reduce the activity of the catalyst. The reaction temperature must therefore be set properly and at the same time HF must be diluted with nitrogen, etc. to control the temperature elevation resulting from the fluorination reaction. Generally, the fluorination temperature ranges from 200°C to 400°C. An aluminum catalyst, particularly with alumina as the material, is preferably be fluorinated until the fluorine content reaches around 50% to 80% (AlF₃ standards). When used in reaction at higher temperatures, fluorination up to about 90% is suggested.

In the chlorine fluorination reaction of hexachloropropene, the mol ratio of hexachloropropene to hydrogen fluoride is 1 : 1 to 1 : 100, preferably 1 : 5 to 1 : 50, and the mol ratio of hexachloropropene to chlorine is 1 : 1 to 1 : 30, preferably 1 : 1 to 1 : 20.

The usable vapor phase reaction methods include the fixed bed vapor phase reaction method and the fluidized vapor phase reaction method.

The reaction temperature may be 50°C to 500°C, normally 100°C to 500°C, and preferably 150°C to 400°C.

Reaction is practicable either atmospheric, reduced, or applied pressure conditions, but reaction under atmospheric or applied pressure conditions is preferred to reduce equipment complexity.

The optimum contact time of hexachloropropene with the catalyst, which depends upon other conditions, is 0.1s to 100s.

In the chlorofluorination of hexachloropropene, CF₃CCl₂CF₂Cl is the target compound, but CF₃CCl₂CCl₂F, CF₃CCl = CFC1, CF₃CCl = CCl₂, compounds which are insufficiently chlorofluorinated, may also be obtained as by-products. Further chlorofluorination can convert these compounds into the intended CF₃CCl₂CF₂Cl. Consequently, these by-products can be reused by returning them to the reaction system.

In the liquid phase method in Method A, chlorofluorinated antimony may be used as a catalyst. chlorofluorinated antimony used in this reaction can be prepared either by reacting antimony pentachloride with hydrogen fluoride to be partially fluorinated, or by reacting antimony trifluoride with chlorine. The fluorine content in halogenated antimony depends upon the reaction conditions, irrespective of the preparation method.

Five-fold mols of HF used in the reaction to hexachloropropene are required theoretically, and reaction is still practicable with five-fold mols; however, in order to improve the reaction it is necessary to increase the reaction quantity of HF in the range from five-fold to ten-fold mols. However, excess HF must be recovered as an unreacted product, and hence the use of HF beyond this range is disadvantageous in terms of cost although the reaction is not affected.

Equivalent mols of chlorine used in the reaction to hexachloropropene are necessary theoretically, and reaction is still practicable with equivalent mols; however, in order to improve the reaction, 1.2 to 3 times as many mols of chlorine is desired be used. In the same way as HF, however, excess chlorine must be recovered as an unreacted product, and hence the introduction of chlorine beyond this range is disadvantageous in terms of cost although the reaction is not affected.

analyzed by gas chromatography. The results are shown in Table 2.

Table 2

Product	Yield rate (%)	
	Example 4	Example 5
$\text{CF}_3\text{CCl}_2\text{CF}_2\text{Cl}$	40	40
$\text{CF}_3\text{CCl}_2\text{CFCl}_2$	44	44
$\text{CF}_3\text{CCl}=\text{CFCl}$		
$\text{CF}_3\text{CCl}=\text{CCl}_2$		

Note that the by-products $\text{CF}_3\text{CCl}_2\text{CFCl}_2$, $\text{CF}_3\text{CCl}=\text{CFCl}$, and $\text{CF}_3\text{CCl}=\text{CCl}_2$ are compounds which can be reused for manufacturing the target product CFC215aa.

Example 6

Synthesis of CFC215aa through chlorofluorination of hexachloropropene by the liquid phase method (1):

29.9 g (0.1 mol) of SbCl_5 was placed in a condenser-equipped autoclave of 500 ml made of Hastelloy. The temperature was then gradually raised to 80°C inside the reactor, in which HF was passed at 0.5 mol/hr for 1 hour.

With the temperature kept at 80°C, 0.5 mol/hr of hexachloropropene, 3 mol/hr of HF, and 1.0 mol/hr of chlorine were added. During the reaction, the reaction pressure was kept at 10 kg/cm². When 498g (2 mol) of hexachloropropene was added, the reaction was stopped. After the reaction was completed, the pressure was gradually reduced and the contents were extracted.

Organic matters which were distilled during the reaction and which remained in the autoclave after the reaction were collectively analyzed by gas chromatography. The results are shown in Table 3.

Example 7

Synthesis of CFC215aa through chlorofluorination of hexachloropropene by the liquid phase method (2):

29.9 g (0.1 mol) of SbCl_5 was placed in a condenser-equipped autoclave of 500 ml made of Hastelloy. The temperature was then gradually raised to 60°C inside the reactor, in which HF was passed at 0.5 mol/hr for 1 hour.

With the temperature kept at 60°C, 0.5 mol/hr of hexachloropropene, 3 mol/hr of HF, and 1.0 mol/hr of chlorine were added. During the reaction, the reaction pressure was kept at 10 kg/cm². When 498 g (2 mol) of hexachloropropene was added, the reaction was stopped. After the reaction was completed, the pressure was gradually reduced, and the contents were extracted.

Organic matters which were distilled during the reaction and which remained in the autoclave after the reaction were collectively analyzed by gas chromatography. The results are shown in Table 3.

Example 8

Synthesis of CFC215aa through chlorofluorination of hexachloropropene by the liquid phase method (3):

29.9 g (0.1 mol) of SbCl_5 was placed in a condenser-equipped autoclave of 500 ml made of Hastelloy. The temperature was then gradually raised to 80°C inside the reactor, through which HF was passed at 0.5 mol/hr for 1 hour.

With the temperature kept at 80°C, 0.5 mol/hr of hexachloropropene, 3 mol/hr of HF, and 1.5 mol/hr of chlorine were added. During the reaction, the reaction pressure was kept at 10 kg/cm². When 249 g (1 mol) of hexachloropropene was added, the reaction was stopped. After the reaction was completed, the pressure was gradually reduced, and the contents were extracted.

Organic matters which were distilled during the reaction and which remained in the autoclave after reaction were collectively analyzed by gas chromatography. The results are shown in Table 3.

Table 3

Product	Yield rate (%)		
	Example 6	Example 7	Example 8
$\text{CF}_3\text{CCl}_2\text{CF}_2\text{Cl}$	85	61	95
$\text{CF}_3\text{CClHCF}_2\text{Cl}$	11	14	4
$\text{CCl}_3\text{CF}=\text{CF}_2$	4	25	1

Example 9

Synthesis of 2,3,3-trichloro-1,1,1-trifluoropropene through fluorination of hexachloropropene by the vapor phase method:

First by the following method, Al_2O_3 was fluorinated. Into a 20 mm diameter reaction tube made of Hastelloy C, 11.5 g (16 cc) of Al_2O_3 in pellet form was filled. The tube was heated from room temperature, while passing nitrogen and hydrogen fluoride, gradually up to the reaction temperature. When the temperature was reached inside the system, the nitrogen was stopped, and when the temperature was stabilized, the chlorofluorination reaction was started.

Through the reaction tube filled with 11.5 g of Al_2O_3 which had been fluorinated, 7 cc/min of prevaporized hexachloropropene and 95 cc/min of hydrogen fluoride were passed to effect the reaction at 300°C. The produced gas was washed with water and the water solution of alkali and then analyzed by gas chromatography. The results are shown in Table 4.

Table 4

Product	Yield rate (%)
$\text{CF}_3\text{CCl}=\text{CCl}_2$	95
$\text{CF}_3\text{CCl}_2\text{CFCl}_2$	3

Through the fluorination reaction, the by-products $\text{CF}_3\text{CCl}_2\text{CFC}_2$ can be reused for manufacturing the target product $\text{CF}_3\text{CCl}_2\text{CF}_2\text{Cl}$.

Example 10

Synthesis of CFC215aa through chlorofluorination of 2,3,3-trichloro-1,1,1-trifluoropropene by the vapor phase method (1):

Through the reaction tube filled with 20 g of Cr_2O_3 which was fluorinated in the same manner as in Example 4, 11 cc/min of prevaporized $\text{CF}_3\text{CCl}=\text{CCl}_2$, 133 cc/min of hydrogen fluoride and 62 cc/min of chlorine were passed to effect the reaction at 200°C. The produced gas was washed with water, alkali and the water solution of reducer, and then analyzed by gas chromatography. The results are shown in Table 5.

Example 11

Synthesis of CFC215aa through chlorofluorination of 2,3,3-trichloro-1,1,1-trifluoropropene by the vapor phase method (2):

Through the reaction tube filled with 20g of Cr_2O_3 which had been fluorinated in the same manner as in Example 4, 11 cc/min of prevaporized $\text{CF}_3\text{CCl}=\text{CCl}_2$, 133 cc/min of hydrogen fluoride and 62 cc/min of chlorine were passed to perform reaction at 250°C. The produced gas was washed with water, alkali and the water solution of the reducer,

and then analyzed by gas chromatography. The results are shown in Table 5.

Table 5

Product	Yield rate (%)	
	Example 10	Example 11
$\text{CF}_3\text{CCl}_2\text{CF}_2\text{Cl}$	30	88
$\text{CF}_3\text{CCl}_2\text{CFCl}_2$	65	2
$\text{CF}_3\text{CCl}=\text{CFCl}$		
$\text{CF}_3\text{CCl}=\text{CCl}_2$		

Note that the by-products $\text{CF}_3\text{CCl}_2\text{CFC1}_2$, $\text{CF}_3\text{CCl}=\text{CFC1}$, and $\text{CF}_3\text{CCl}=\text{CCl}_2$ can be reused for manufacturing the target product $\text{CF}_3\text{CCl}_2\text{CF}_2\text{Cl}$.

Example 12

Synthesis of CFC215aa through chlorofluorination of 2,3,3-trichloro-1,1,1-trifluoropropene by the liquid phase method:

29.9 g (0.1 mol) of SbCl_5 was placed in a condenser-equipped autoclave of 500 ml made of Hastelloy. The temperature was then gradually raised to 80°C inside the reactor, in which HF was passed at 0.5 mol/hr for 1 hour.

With the temperature kept at 80°C, 0.5 mol/hr of 2,3,3-trichloro-1,1,1-trifluoropropene, 3 mol/hr of HF, and 1.5 mol/hr of chlorine were added. During the reaction, the reaction pressure was kept at 10 kg/cm².

When 200 g (1 mol) of 2,3,3-trichloro-1,1,1-trifluoropropene was added, the reaction was stopped. After the reaction was completed, the pressure was gradually reduced and the contents were extracted.

Organic matters which were distilled during the reaction and which remained in the autoclave after the reaction were collectively analyzed by gas chromatography. The results are shown in Table 6.

Table 6

Product	Yield rate (%)
$\text{CF}_3\text{CCl}_2\text{CF}_2\text{Cl}$	93
$\text{CF}_3\text{CClHCF}_2\text{Cl}$	6
$\text{CClCF}=\text{CF}_2$	1

Example 13

Synthesis of CFC215aa through chlorofluorination of propane by the vapor phase method (1):

First by the following method, Cr_2Cl_3 was carried on active carbon. 1.8 g of $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ was dissolved in 12 cc of ion-exchanged water, to which 6 g (14 cc) of active carbon was added. After allowing to stand overnight at room temperature, the water content was removed by an evaporator and it was then allowed to dry another night at 120°C.

Then, active carbon carrying CrCl_3 was fluorinated. The catalyst thus obtained was filled into a 20 mm diameter reaction tube made of Hastelloy C. The tube was then heated from room temperature in an electric furnace, while passing nitrogen and hydrogen fluoride, gradually up to the reaction temperature (350°C). When the temperature was reached inside the system, the nitrogen was stopped, and when the temperature was stabilized, the chlorofluorination reaction was started.

Through the reaction tube filled with 6 g of active carbon carrying CrCl_3 which had been fluorinated, 6 cc/min of propane, 96 cc/min of hydrogen fluoride and 66 cc/min of chlorine were passed to effect the reaction at 350°C. The produced gas was washed with water, alkali, and the water solution of reducer, and then analyzed by gas chromatography. The results are shown in Table 7.

Example 14

Synthesis of CFC215aa through chlorofluorination of propane by the vapor phase method (2):

First by the following method, FeCl_3 was carried on active carbon. 1.8 g of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ was dissolved in 12 cc of ion-exchanged water, to which 6 g (14 cc) of active carbon was added. After allowing to stand overnight at room temperature, the water content was removed by an evaporator and it was then allowed to dry another night at 120°C .

Then, active carbon carrying FeCl_3 was fluorinated. The catalyst thus obtained was filled into a 20 mm diameter reaction tube made of Hastelloy C. The tube was heated from room temperature in an electric furnace, while passing nitrogen and hydrogen fluoride, gradually up to the reaction temperature (400°C). When the temperature was reached inside the system, the nitrogen was stopped, and when the temperature was stabilized, the chlorofluorination reaction was started.

Through the reaction tube filled with 6 g of active carbon carrying the above FeCl_3 which had been fluorinated, 6 cc/min of propane, 106 cc/min of hydrogen fluoride and 55 cc/min of chlorine were passed to effect the reaction at 400°C . The produced gas was washed with water, alkali, and the water solution of reducer, and then analyzed by gas chromatography. The results are shown in Table 7.

Table 7

Product	Yield rate (%)	
	Example 13	Example 14
$\text{CF}_3\text{CCl}_2\text{CF}_2\text{Cl}$	40	43
$\text{CF}_3\text{CCl}_2\text{CFCl}_2$	45	45
$\text{CF}_3\text{CCl}=\text{CFCl}$		
$\text{CF}_3\text{CCl}=\text{CCl}_2$		

Note that the by-products $\text{CF}_3\text{CCl}_2\text{CFCl}_2$, $\text{CF}_3\text{CCl}=\text{CFCl}$, and $\text{CF}_3\text{CCl}=\text{CCl}_2$ can be reused for manufacturing the target product $\text{CF}_3\text{CCl}_2\text{CF}_2\text{Cl}$.

Example 15

Synthesis of 2,3,3-trichloro-1,1,1-trifluoropropene through chlorofluorination of propane by the vapor phase method:

First by the following method, CuCl_2 was carried on active carbon. 0.9 g of CuCl_2 was dissolved in 12 cc of ion-exchanged water, to which 6 g (14 cc) of active carbon was added. After allowing to stand overnight at room temperature, the water content was removed by an evaporator, and it was then allowed to dry another night at 120°C .

Then, active carbon carrying CuCl_2 was fluorinated. The catalyst thus obtained was filled into a 20 mm diameter reaction tube made of Hastelloy C. The tube was heated from room temperature in an electric furnace, while passing nitrogen and hydrogen fluoride, gradually up to the reaction temperature (400°C). When the temperature was reached inside the system, the nitrogen was stopped, and when the temperature was stabilized, the chlorofluorination reaction was started.

Through the reaction tube filled with 6 g of active carbon carrying CuCl_2 which had been fluorinated, 6 cc/min of propane, 106 cc/min of hydrogen fluoride, and 55 cc/min of chlorine were passed to effect the reaction at 400°C . The produced gas was washed with water, alkali, and the water solution of reducer, and then analyzed by gas chromatography. The results are shown in Table 8 below.

Table 8

Product	Yield rate (%)
$\text{CF}_3\text{CCl}=\text{CCl}_2$	84
$\text{CF}_3\text{CCl}_2\text{CFCl}_2$	2

Note that the by-product $\text{CF}_3\text{CCl}_2\text{CFCl}_2$ is a compound which can be reused for manufacturing the target product $\text{CF}_3\text{CCl}_2\text{CF}_2\text{Cl}$.

Example 16

Synthesis of HFC245fa through reduction of CFC215aa:

When the 2,2,3-trichloro-1,1,1,3,3-pentafluoropropane obtained in Examples 4 to 15 was reduced with hydrogen in the same manner as described in Example 1, then 1,1,1,3,3-pentafluoropropane was obtained at the conversion yield and selectivity rates given in Example 1. When the hydrogen reduction was performed in the same manner as described in Examples 2 and 3, the same results as in Examples 2 and 3 were obtained.

The above results show that based on the methods of this invention, a starting substance, which can be obtained at relatively low cost, can be used to produce 2,2,3-trichloro-1,1,1,3,3-pentafluoropropane with a high yield rate. Many of the generated by-products can be reused as raw materials for manufacturing 2,2,3-trichloro-1,1,1,3,3-pentafluoropropane. Furthermore, 1,1,1,3,3-pentafluoropropane can be efficiently and economically manufactured since 2,2,3-trichloro-1,1,1,3,3-pentafluoropropane can be efficiently reduced to 1,1,1,3,3-pentafluoropropane.

Claims

1. A method of producing 1,1,1,3,3-pentafluoropropane including a process in which 2,2,3-trichloro-1,1,1,3,3-pentafluoropropane is allowed to react with not less than 4.5 equivalent parts of hydrogen to 2,2,3-trichloro-1,1,1,3,3-pentafluoropropane in the presence of a noble metal catalyst by the vapor phase method to be hydrogen-reduced.

2. The production method described in Claim 1, in which a catalyst selected from palladium, platinum and rhodium is used as the noble metal catalyst.

3. The production method described in Claim 2, in which 4.5 to 10 equivalent parts of hydrogen are used to 2,2,3-trichloro-1,1,1,3,3-pentafluoropropane.

4. The production method described in Claim 2 or 3, in which a palladium catalyst is carried on a carrier composed of at least one of active carbon, alumina, silica gel, titanium oxide and zirconia.

5. The production method described in Claim 4, in which the carrying concentration of the palladium catalyst on the carrier is 0.05% to 10% by weight.

6. The production method described in any of Claims 2 to 5, in which the reaction is effected at a temperature from 100°C to 350°C.

7. A method of producing 1,1,1,3,3-pentafluoropropane including processes (1) and (2) as follows:

(1) A process in which hexachloropropene is allowed to react with hydrogen fluoride and chlorine in the presence of chromium and/or aluminum catalyst(s) by the vapor phase method, or in the presence of an antimony catalyst by the liquid phase method to obtain 2,2,3-trichloro-1,1,1,3,3-pentafluoropropane.

(2) A process in which this 2,2,3-trichloro-1,1,1,3,3-pentafluoropropane is allowed to react with not less than 4.5 equivalent parts of hydrogen to this 2,2,3-trichloro-1,1,1,3,3-pentafluoropropane in the presence of a noble metal catalyst by the vapor phase method to be hydrogen-reduced, obtaining 1,1,1,3,3-pentafluoropropane.

8. A method of producing 1,1,1,3,3-pentafluoropropane including processes (1), (2) and (3) as follows:

(1) A process in which hexachloropropene is allowed to react with hydrogen fluoride in the presence of an aluminum catalyst by the vapor phase method to obtain 2,3,3-trichloro-1,1,1-trifluoropropene.

(2) A process in which this 2,3,3-trichloro-1,1,1-trifluoropropene is allowed to react with hydrogen fluoride and chlorine in the presence of at least one metal catalyst selected from a group composed of chromium, iron, cobalt, zinc, copper and manganese by the vapor phase method, or in the presence of an antimony catalyst by the liquid phase method to obtain 2,2,3-trichloro-1,1,1,3,3-pentafluoropropane.

(3) A process in which this 2,2,3-trichloro-1,1,1,3,3-pentafluoropropane is allowed to react with not less than 4.5 equivalent parts of hydrogen to 2,2,3-trichloro-1,1,1,3,3-pentafluoropropane in the presence of a noble metal catalyst by the vapor phase method to be hydrogen-reduced, obtaining 1,1,1,3,3-pentafluoropropane.

9. A method of producing 1,1,1,3,3-pentafluoropropane including processes (1) and (2) as follows:

(1) A process in which at least one of 2,3,3-trichloro-1,1,1-trifluoropropene, 1,2,3,3-tetrachloro-1,1-difluoropropene, and 1,1,2,3,3-pentachloro-1-fluoropropene is allowed to react with hydrogen-fluoride and chlorine in the presence of at least one metal catalyst selected from a group composed of chromium, iron, cobalt, zinc, copper and manganese by the vapor phase method, or in the presence of an antimony catalyst by the liquid phase method to obtain 2,2,3-trichloro-1,1,1,3,3-pentafluoropropane.

(2) A process in which this 2,2,3-trichloro-1,1,1,3,3-pentafluoropropane is allowed to react with not less than 4.5 equivalent parts of hydrogen to 2,2,3-trichloro-1,1,1,3,3-pentafluoropropane in the presence of a noble metal catalyst by the vapor phase method to be hydrogen-reduced, obtaining 1,1,1,3,3-pentafluoropropane.

10. A method of producing 1,1,1,3,3-pentafluoropropane including processes (1) and (2) as follows:

(1) A process in which at least one compound selected from a group composed of propane, propylene, and partially halogenated acyclic hydrocarbon having 3 carbons is allowed to react with hydrogen fluoride and chlorine in the presence of chromium and/or iron catalyst(s) by the vapor phase method to obtain 2,2,3-trichloro-1,1,1,3,3-pentafluoropropane.

(2) A process in which this 2,2,3-trichloro-1,1,1,3,3-pentafluoropropane is allowed to react with not less than 4.5 equivalent parts of hydrogen to 2,2,3-trichloro-1,1,1,3,3-pentafluoropropane in the presence of a noble metal catalyst by the vapor phase method to be hydrogen-reduced, obtaining 1,1,1,3,3-pentafluoropropane.

11. A method of producing 1,1,1,3,3-pentafluoropropane including processes (1), (2) and (3) as follows:

(1) A process in which at least one compound selected from a group composed of propane, propylene, and partially halogenated acyclic hydrocarbon having 3 carbons is allowed to react with hydrogen fluoride and chlorine in the presence of at least one metal catalyst selected from a group composed of aluminum, copper, cobalt, zinc and manganese by the vapor phase method to obtain 2,3,3-trichloro-1,1,1-trifluoropropene.

(2) A process in which this 2,3,3-trichloro-1,1,1-trifluoropropene is allowed to react with hydrogen fluoride and chlorine in the presence of at least one metal catalyst selected from a group composed of chromium, iron, cobalt, zinc, copper and manganese by the vapor phase method, or in the presence of an antimony catalyst by the liquid phase method to obtain 2,2,3-trichloro-1,1,1,3,3-pentafluoropropane.

(3) A process in which this 2,2,3-trichloro-1,1,1,3,3-pentafluoropropane is allowed to react with not less than 4.5 equivalent parts of hydrogen to 2,2,3-trichloro-1,1,1,3,3-pentafluoropropane in the presence of a noble metal catalyst by the vapor phase method to be hydrogen-reduced, obtaining 1,1,1,3,3-pentafluoropropane.

12. A method of producing 2,2,3-trichloro-1,1,1,3,3-pentafluoropropane including a process in which hexachloropropene is allowed to react with hydrogen fluoride and chlorine in the presence of chromium and/or aluminum catalyst(s) by the vapor phase method, or in the presence of an antimony catalyst by the liquid phase method.

13. A method of producing 2,2,3-trichloro-1,1,1,3,3-pentafluoropropane including processes (1) and (2) as follows:

(1) A process in which hexachloropropene is allowed to react with hydrogen fluoride in the presence of an aluminum catalyst by the vapor phase method to obtain 2,3,3-trichloro-1,1,1-trifluoropropene.

(2) A process in which this 2,3,3-trichloro-1,1,1-trifluoropropene is allowed to react with hydrogen fluoride and chlorine in the presence of at least one metal catalyst selected from a group composed of chromium, iron, cobalt, zinc, copper and manganese by the vapor phase method, or in the presence of an antimony catalyst by the liquid phase method to obtain 2,2,3-trichloro-1,1,1,3,3-pentafluoropropane.

14. A method of producing 2,2,3-trichloro-1,1,1,3,3-pentafluoropropane including a process in which at least one of 2,3,3-trichloro-1,1,1-trifluoropropene, 1,2,3,3-tetrachloro-1,1-difluoropropene, and 1,1,2,3,3-pentachloro-1-fluoropropene is allowed to react with hydrogen fluoride and chlorine in the presence of at least one metal catalyst selected from a group composed of chromium, iron, cobalt, zinc, copper, and manganese by the vapor phase method, or in the presence of an antimony catalyst by the liquid phase method to obtain 2,2,3-trichloro-1,1,1,3,3-pentafluoropropane.

15. A method of producing 2,3,3-trichloro-1,1,1-trifluoropropene including a process in which hexachloropropene is allowed to react with hydrogen fluoride in the presence of an aluminum catalyst by the vapor phase method.

16. The production method described in any of Claims 7, 8, 11, 12, 13, and 15, in which the catalyst is carried on a carrier at a concentration of not less than 0.1% by weight in the chlorofluorination or fluorination of hexachloropropene.

17. The production method described in any of Claims 7, 8, 11, 12, 13 and 15 in which the catalyst is fluorinated prior to starting the reaction in the chlorofluorination or fluorination of hexachloropropene.
- 5 18. The production method described in any of Claims 7, 8, 11, 12, 13 and 15, in which the mole ratio of hexachloropropene to hydrogen fluoride is 1 : 1 to 1 : 100, and that of hexachloropropene to chlorine is 1 : 1 to 1 : 30 in the chloro-fluorination or fluorination of hexachloropropene.
- 10 19. The production method described in any of Claims 7, 8, 11, 12, 13 and 15, in which the chlorofluorination or fluorination reaction temperature of hexachloropropene is 50°C to 500°C.
- 20 20. The production method described in Claim 8 or 13, in which the catalyst is carried on a carrier at a concentration of 0.1% to 50% by weight in the chlorofluorination of 2,3,3-trichloro-1,1,1-trifluoropropene.
- 15 21. The production method described in Claim 8 or 13 in which the catalyst is fluorinated prior to starting the reaction in the chlorofluorination of 2,3,3-trichloro-1,1,1-trifluoropropene.
- 20 22. The production method described in Claim 8 or 13, in which the mole ratio of 2,3,3-trichloro-1,1,1-trifluoropropene to hydrogen fluoride is 1 : 1 to 1 : 50, and that of 2,3,3-trichloro-1,1,1-trifluoropropene to chlorine is 1 : 1 to 1 : 30 in the chlorofluorination of 2,3,3-trichloro-1,1,1-trifluoropropene.
- 25 23. The production method described in Claim 8 or 13, in which the chlorine-fluorination reaction temperature of 2,3,3-trichloro-1,1,1-trifluoropropene is 50°C to 500°C.
- 25 24. The production method described in any of Claims 9 to 11, and 14, in which the catalyst is carried on a carrier at a concentration of 0.1% to 50% by weight in the chlorofluorination of the starting substance.
- 30 25. The production method described in any of Claims 9 to 11, and 14, in which the catalyst is fluorinated prior to starting the reaction in the chlorofluorination of the starting substance.
- 30 26. The production method described in Claim 9 or 14, in which the mole ratio of the starting substance to hydrogen fluoride is 1 : 1 to 1 : 50, and that of the starting substance to chlorine is 1 : 1 to 1 : 30 in the chlorine-fluorination of the starting substance.
- 35 27. The production method described in any of Claims 9 to 11 and 14 in which the chlorofluorination reaction temperature of the starting substance is 50°C to 500°C.
- 40 28. The production method described in Claim 10 or 11, in which the mole ratio of the starting substance to hydrogen fluoride is 1 : 5 to 1 : 100, and that of the starting substance to chlorine is 1 : 5 to 1 : 30 in the chlorofluorination of the starting substance.
- 45 29. The production method described in Claim 11, in which 4.5 to 10 equivalent parts of hydrogen are used to 2,2,3-trichloro-1,1,1,3,3-pentafluoropropane.
30. The production method described in Claim 11, in which the noble metal catalyst is carried on the carrier composed of at least one of active carbon, alumina, silica gel, titanium oxide and zirconia.
31. The production method described in Claim 11, in which the carrying concentration of the noble metal catalyst on the carrier is 0.05% to 10% by weight.
- 50 32. The production method described in Claim 11, in which the reaction is performed in the temperature range from 100°C to 350°C.

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP94/00867

A. CLASSIFICATION OF SUBJECT MATTER Int. C15 C07C19/08, 21/18, 17/00, 17/10, 17/20, B01J23/42, 23/44, 23/46, 21/04, 23/26, 27/10, 27/132, 27/122, 27/128 According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) Int. C15 C07C19/08, 21/18, 17/00, 17/10, 17/20, B01J23/42, 23/44, 23/46, 21/04, 23/26, 27/10, 27/132, 27/122, 27/128 Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) CAS ONLINE		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JP, A, 4-108746 (E.I. Du Pont de Nemours and Co.), April 9, 1992 (09. 04. 92), Lines 5 to 10, page 21, line 25, page 21 to line 1, page 22, lines 16 to 20, page 23	12, 14, 18-19, 22-23, 26-27
A	& EP, A1, 434408 & US, A, 5068472	7, 16-17, 20-21, 24-25, 28-32
A	US, A, 2942036 (Allied Chemical Corporation), June 21, 1960 (21. 06. 60), Example 1-3	1-11, 20-32
A	JP, A, 4-145033 (E. I. Du Pont de Nemours and Co.), May 19, 1992 (19. 05. 92), Example 48 & EP, A1, 434409 & US, A, 5057634	10-11, 24-32
A	US, A, 2558703 (Hooker Electrochemical Company) June 26, 1951 (26. 06. 51)	13, 15-17, 20-23
<input type="checkbox"/> Further documents are listed in the continuation of Box C. <input type="checkbox"/> See patent family annex.		
* Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family		
Date of the actual completion of the international search September 9, 1994 (09. 09. 94)		Date of mailing of the international search report October 11, 1994 (11. 10. 94)
Name and mailing address of the ISA/ Japanese Patent Office Facsimile No.		Authorized officer Telephone No.

Form PCT/ISA/210 (second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP94/00867

Box I Observations where certain claims were found unsearchable (Continuation of Item 1 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of Item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

- A. Claims 1 to 11 and 28 to 32 each relates to a process for producing 1,1,1,3,3-pentafluoropropane comprising the step of reducing 2,2,3-trichloro-1,1,1,3,3-pentafluoropropane with hydrogen.
 - B. Claim 12 relates to a process for producing 2,2,3-trichloro-1,1,1,3,3-pentafluoropropane comprising the step of reacting hexachloropropene with hydrogen fluoride and chlorine.
1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
 2. ☒ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
 3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

 4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
- ☐ No protest accompanied the payment of additional search fees.

Form PCT/ISA/210 (continuation of first sheet (1)) (July 1992)

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP94/00867

Continuation of Box No. II

- C. Claims 13 and 14 each relates to a process for producing 2,2,3-trichloro-1,1,1,3,3-pentafluoropropane comprising the step of reacting 2,3,3-trichloro-1,1,1-trifluoropropene with hydrogen fluoride and chlorine.
- D. Claim 15 relates to a process for producing 2,3,3-trichloro-1,1,1-trifluoropropene comprising the step of reacting hexachloropropene with hydrogen fluoride.
- E. Claims 16 to 19 each includes the above inventions A, B, C and D.
- F. Claims 20 to 23 each includes the above inventions A and C.
- G. Claims 24 to 27 each includes the above inventions A and C.

And because the inventions A, B, C and D respectively relate to processes for producing different compounds through different steps, these four groups of inventions are not considered as relating to a group of inventions so linked as to form a single general inventive concept.

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